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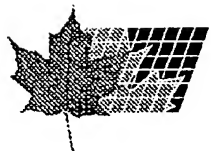
(54) DETERSIF POUR LAVE-VAISSELLE SOUS FORME SOLIDE AYANT UNE SOLUBILITE SPECIFIQUE

(54) DISHWASHER DETERGENT SHAPED BODIES WITH SPECIFIC SOLUBILITY

(57)

The invention relates to deterative shaped bodies with high storage stability, minimal packaging volume, a good fragrance profile and a defined solubility profile. In the shaped bodies, there is a defined region which contains more than 80% by weight, preferably more than 90% by weight, more preferably more than 95% by weight and, most preferably, 100% by weight of an ingredient (I) present. This defined region dissolves more than 5%, preferably more than 10%, more preferably more than 25%, most preferably more than 50% and, in one particularly advantageous embodiment, more than 100% faster than the remaining region and/or regions of the shaped body.

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(54) **DETERSIF POUR LAVE-VAISSELLE SOUS FORME SOLIDE  
AYANT UNE SOLUBILITE SPECIFIQUE**  
(54) **DISHWASHER DETERGENT SHAPED BODIES WITH  
SPECIFIC SOLUBILITY**

(57) The invention relates to detergent shaped bodies with high storage stability, minimal packaging volume, a good fragrance profile and a defined solubility profile. In the shaped bodies, there is a defined region which contains more than 80% by weight, preferably more than 90% by weight, more preferably more than 95% by weight and, most preferably, 100% by weight of an ingredient (I) present. This defined region dissolves more than 5%, preferably more than 10%, more preferably more than 25%, most preferably more than 50% and, in one particularly advantageous embodiment, more than 100% faster than the remaining region and/or regions of the shaped body.



### **Abstract**

The invention relates to deterative shaped bodies with high storage stability, minimal packaging volume, a good fragrance profile and a defined solubility profile. In the shaped bodies, there is a defined region which contains more than 80% by weight, preferably more than 90% by weight, more preferably more than 95% by weight and, most preferably, 100% by weight of an ingredient (I) present. This defined region dissolves more than 5%, preferably more than 10%, more preferably more than 25%, most preferably more than 50% and, in one particularly advantageous embodiment, more than 100% faster than the remaining region and/or regions of the shaped body.

Dishwasher Detergent Shaped Bodies with Specific Solubility

This invention relates to deterative shaped bodies, primarily tablets, such as dishwasher tablets, laundry detergent tablets, bleach tablets, stain remover tablets or water softening tablets, for use in the home, more particularly for use in machines, to a process for their production and to  
5 their use.

Deterative shaped bodies, more particularly tablets, have a number of advantages over powder-form compositions, such as easy handling, simple dosage and low packaging volumes.

Unfortunately, problems arise out of the fact that, to achieve  
10 adequate dimensional stability and fracture resistance, relatively high pressures have to be applied in the compression of the powder-form ingredients. In view of the heavy compaction which they undergo, corresponding tablets often show inadequate storage stability in regard to sensitive ingredients (bleaching agent, perfume, enzymes, silver  
15 protectors, dyes, surfactants), reduced performance (particularly against such soils as tea, milk, starch) by comparison with comparable amounts of active ingredient made up in another form, occasionally inadequate protection of sensitive materials to be cleaned and impaired disintegration and dissolving properties in use.

20 According to some patents belonging to the prior art, some of these problems are said to have been solved.

In many cases, however, the consumer is unable to reproduce the performance advantages described in those documents. Accordingly, an important problem confronting manufacturers of deterative shaped bodies is  
25 to satisfy the consumer.

Accordingly, the problem addressed by the present invention was to provide high-performance, easy-to-handle deterative shaped bodies, above all dishwasher tablets, laundry detergent tablets, stain remover tablets or water softener tablets for use in the home, more particularly for use in

machines, with high storage stability, minimal packaging volume, a good fragrance profile and a defined solubility profile which, above all, would guarantee high consumer satisfaction.

This problem has surprisingly been solved by a shaped body in  
5 which an ingredient (I) is mainly located in a defined region, this region dissolving more quickly than the other region(s) of the shaped body.

Accordingly, the present invention relates to a shaped body containing builders, bleaching agents and surfactants, characterized in that at least one region containing more than 80% by weight, preferably more  
10 than 90% by weight, more preferably more than 95% by weight and, most preferably, 100% by weight of an ingredient (I) present, which dissolves more than 5%, preferably more than 10%, more preferably more than 25%, most preferably more than 50% and, in one particularly advantageous embodiment, more than 100% faster than the remaining region and/or  
15 regions of the shaped body, is present.

The shaped body according to the invention consists of several, i.e. at least two, regions which have different compositions and which therefore dissolve at different rates when the shaped body is introduced into water. The regions may assume various three-dimensional forms and may be  
20 embodied, for example, in layers. However, so-called "ring/core" tablets or "core/jacket" tablets may also be produced with the features according to the invention, one region being formed by the core and the other region by the ring or jacket surrounding the core. Besides the shaped bodies mentioned, which consist of two regions, it is of course also possible to  
25 produce shaped bodies of three or four regions. One example of a shaped body of three regions – besides the simplest embodiment, the three-layer tablet – is a two-layer tablet into which a recess to be subsequently filled with the third region is pressed. Shaped bodies consisting of three regions can be industrially produced by means of suitable tableting machine  
30 providing the press has three filling stations.

More than 80% by weight, preferably more than 90% by weight,

more preferably more than 95% by weight and most preferably 100% by weight is present in the faster dissolving region according to the invention. This means that at least 80% by weight of the total quantity of a certain ingredient referred to herein as "ingredient (I)" is present in the faster  
5 dissolving region. If, for example, a two-layer detergent shaped body contains in all (i.e. based on the weight of the shaped body) 10 g of an ingredient I (for example chlorine bleaching agent), shaped bodies according to the invention are characterized in that more than 8 g of the chlorine bleaching agent (preferably more than 9 g, more preferably more  
10 than 9.5 g and most preferably 10 g) is present in the faster dissolving layer.

The faster dissolving region of the shaped body according to the invention dissolves more than 5%, preferably more than 10%, more preferably more than 25%, most preferably more than 50% and, in one  
15 particularly advantageous embodiment, more than 100% faster than the remaining region and/or regions of the shaped body. In the case of a two-layer tablet, this may be illustrated by the following example: if the slower dissolving layer has a solubility of 20 grams per liter and hour [ $\text{gl}^{-1}\text{h}^{-1}$ ], for example at a given temperature, the faster dissolving region – in  
20 accordance with the present invention – has a solubility of more than  $21 \text{ gl}^{-1}\text{h}^{-1}$  (105%, based on the basic value of 20). In this example, the solubility of the faster dissolving region is more than  $22 \text{ gl}^{-1}\text{h}^{-1}$ , preferably more than  $25 \text{ gl}^{-1}\text{h}^{-1}$ , more preferably more than  $30 \text{ gl}^{-1}\text{h}^{-1}$  and most preferably more than  $40 \text{ gl}^{-1}\text{h}^{-1}$ . Since the solubility of the individual regions of the shaped  
25 body is also temperature-dependent and since the expression "faster dissolving" is based on the dissolving time of the slower dissolving region and can shift with temperature, the solubility values used in the context of the present invention are based on a water temperature of 20°C. If a shaped body according to the invention consists of more than two regions,  
30 two cases are basically possible: the faster dissolving region dissolves faster than the other two regions which have the same solubility values or

the solubility values of the two slower dissolving regions are different. In the latter case, the expression "faster dissolving" is based on the total solubility of the other regions, i.e. in a given volume on the effective reduction in the tablet weight (residual weight without the faster dissolving region) per unit of time. If a constant volume (for example one liter) is used, the dissolving rate in grams per unit of time is directly obtained from the reduction in weight of the shaped body. The above-mentioned unit  $\text{g l}^{-1} \text{h}^{-1}$  is not normally used, instead the unit of measure is minutes or seconds.

10        The ingredient (I) may be a bleaching agent from the group of chlorine and/or oxygen bleaching agents, a bleach activator, a silver protector and/or a soil-release compound, an enzyme, a surfactant or a component or a compound for controlling solubility. However, the ingredient (I) may also be a mixture of these components.

15        In one particularly preferred embodiment, the ingredient (I) is a mixture of a component or a compound for controlling solubility and at least one other ingredient from the group consisting of bleaching agent and/or bleach activator and/or silver protector and/or soil-release compound and/or enzyme and/or a surfactant.

20        The volume of the region containing the ingredient (I), the solubility, the surface and the nature of the compression can also have a critical bearing on the properties of the tablet.

      According to the invention, it can also be favorable if the region containing the ingredient (I) makes up no more than 40% by volume, preferably between 1 and 30% by volume, more preferably between 2 and 25% by volume and more preferably between 3 and 20% by volume of the shaped body.

      It can also be very favorable if the region containing the ingredient (I) occupies no more than 40% of the surface, preferably between 5 and 30%, more preferably between 10 and 25% and most preferably between 15 and 20% by volume of the shaped body.



### Solubility

The solubility can be influenced by components and/or compounds for accelerating solubility (disintegrators) or retarding solubility.

5        Suitable disintegrators are any of the disintegrators known from the prior art. Particular reference is made in this regard to *Römpp (9th Edition, Vol. 6, page 4440)* and *Voigt "Lehrbuch der pharmazeutischen Technologie" (6th Edition, 1987)*. Particularly suitable disintegrators are such materials as starch, cellulose and cellulose derivatives, alginates,  
10        dextrans, crosslinked polyvinyl pyrrolidones and others; systems of weak acids and carbonate-containing disintegrators, more particularly citric acid and tartaric acid in combination with hydrogen carbonate or carbonate and polyethylene glycol sorbitan fatty acid ester.

      According to International patent application **WO-A-96/06156** also, it  
15        can be of advantage to incorporate disintegrators in detergent tablets. In this case, too, typical disintegrators are said to include microcrystalline cellulose, sugars, such as sorbitol, and layered silicates, more particularly fine-particle and swellable layered silicates of the bentonite and smectite type. Effervescent substances, such as citric acid, bisulfate, bicarbonate,  
20        carbonate and percarbonate, are also mentioned as possible disintegration aids.

      European patent applications **EP-A-0 466 485**, **EP-A-0 522 766**, **EP-A-0 711 827**, **EP-A-0 711 828** and **EP-A-0 716 144** describe the production of deterative tablets in which compacted particulate material with a particle  
25        size of 180 to 2000  $\mu\text{m}$  is used. The resulting tablets may have both a homogeneous structure and a heterogeneous structure. According to **EP-A-0 522 766**, at least those particles which contain surfactants and builders are coated with a solution or dispersion of a binder/disintegration aid, more particularly polyethylene glycol. Other binders/disintegration aids are -  
30        again - the already repeatedly described and known disintegrators, for example starches and starch derivatives, commercially available cellulose

derivatives, such as crosslinked and modified cellulose, microcrystalline cellulose fibers, crosslinked polyvinyl pyrrolidones, layered silicates, etc. Weak acids, such as citric acid or tartaric acid which, in conjunction with carbonate-containing sources, lead to effervescent effects on contact with water and which, according to Römpp's definition, belong to the second class of disintegrators, may also be used as a coating material.

Particular reference is made to hitherto unpublished **DE 197 10 254** which describes disintegrators of which the particle size distribution (sieve analysis) is such that at most 1% by weight, preferably less, of dust is present and a total (including any dust present) of less than 10% by weight of the disintegrator granules are smaller than 0.2 mm. At least 90% by weight of the disintegrator granules advantageously have a particle size of at least 0.2 mm and at most 3 mm. These disintegrators are particularly suitable for the purposes of the present invention. Detergent shaped bodies containing granular or optionally co-granulated disintegrators are also described in German patent application **DE 197 09 991** (Stefan Herzog) and in International patent application **WO98/40463** (Henkel). These documents also contain details of the production of granulated, compacted or co-granulated cellulose disintegrators. The particle sizes of such disintegrators is generally above 200  $\mu\text{m}$ , at least 90% by weight of the disintegrators preferably being between 300 and 1600  $\mu\text{m}$  in size and, more preferably, between 400 and 1200  $\mu\text{m}$  in size. The relatively coarse cellulose-based disintegrators mentioned above and described in detail in the cited documents are preferably used as disintegrators in accordance with the present invention and are commercially available, for example, under the name of Arbocel® TF-30-HG from Rettenmaier.

Disintegrators belonging to the group of organic acids, for example citric acid, or a citric acid/bicarbonate mixture and/or the celluloses and cellulose derivatives are also suitable. If a disintegrator is present in the shaped body, the dissolving time of the shaped body as a whole is preferably shorter than the duration of the main wash cycle of a

conventional dishwashing machine, i.e. shorter than 40 mins., preferably shorter than 30 mins., more preferably shorter than 20 mins., and most preferably shorter than 10 mins.

In a particularly preferred embodiment of the invention, the faster  
5 dissolving region contains at least one acidifying agent. Suitable acidifying agents are, for example, boric acid and alkali metal hydrogen sulfates, alkali metal dihydrogen phosphates and other inorganic salts. However, organic acidifying agents are preferably used, citric acid being a particularly preferred acidifying agent. However, other solid mono-, oligo- and  
10 polycarboxylic acids in particular may also be used. Within this group, tartaric acid, succinic acid, malonic acid, adipic acid, maleic acid, fumaric acid, oxalic acid and polyacrylic acid are preferred. Organic sulfonic acids, such as amidosulfonic acid, may also be used. Sokalan® DCS (trademark of BASF), a mixture of succinic acid (max. 31% by weight), glutaric acid  
15 (max. 50% by weight) and adipic acid (max. 33% by weight), is commercially obtainable and may also be used with advantage as an acidifying agent for the purposes of the present invention.

According to the invention, preferred detergent shaped bodies are those in which an acidifying agent selected from the group of organic di-,  
20 tri- and oligocarboxylic acids or mixtures thereof is present in the faster dissolving region, citric acid being particularly preferred. The acidifying agents mentioned are preferably either sole components I or at least a part thereof. Accordingly, in a preferred embodiment of the invention, at least 80% by weight, preferably more than 90% by weight, more preferably more  
25 than 95% by weight and, most preferably, 100% by weight of the acidifying agent present in the shaped body is present in the faster dissolving region.

In preferred embodiments of the present invention, the faster dissolving region may contain - besides the acidifying agent - other ingredients to which the criterion relevant to the ingredient I may also be  
30 advantageously applied, i.e. at least 80% by weight, preferably more than 90% by weight, more preferably more than 95% by weight and most

preferably 100% by weight of these ingredients, too, is contained in the faster dissolving region. These other ingredients are, for example, carbonates and/or hydrogen carbonates of which the use in combination with an acidifying agent leads to the evolution of gas on contact with water  
5 which further reduces the dissolving times. An effervescent system such as this may be formulated with an excess of acidifying agent, so that an acidic prerinse cycle is possible, although other ingredients may also be incorporated in the faster dissolving region, so that the effervescent system releases the other ingredients more quickly. If effervescent systems are  
10 used, the dissolving time of the faster dissolving region is still preferably below the values mentioned above, i.e. below 10 mins., preferably below 5 mins. and more preferably below 2 mins. Quick-dissolving regions such as these can produce distinct advantages in regard to cleaning performance.

In general, paraffins and/or microwaxes and/or the high molecular  
15 weight polyethylene glycols described in detail in the prior art are normally used as dissolution retarders. The use of mixtures mentioned in hitherto unpublished DE 197 27 073, of which the disclosure is hereby specifically included as part of the present disclosure, is particularly suitable for the purposes of the present application.

20 If the shaped body contains a component for retarding solubility, the dissolving time of the shaped body as a whole in cold (20°C) water - in one preferred embodiment - is longer than the prerinse cycle of a commercially available dishwashing machine, i.e. longer than 5 mins. and preferably longer than 10 mins. In cases such as these, a relatively small region of  
25 the shaped body may be dissolution-retarded, so that the greater part of the shaped body makes up the faster dissolving region. By adopting such measures for delaying dissolution, certain ingredients, for example, are only released in the final rinse cycle which affords further advantages in regard to cleaning performance.

### General forms of presentation

The shaped body may assume any of the various three-dimensional forms which are listed inter alia in patents belonging to the prior art and in the standard works of the specialist literature (for example: **Riedel**, "Die  
5 Tablette"). The region in which the ingredient (I) is contained is also not confined to any particular three-dimensional form. However, a dimension in one direction in space of more than 5 mm is preferred for practical reasons.

### 10 Specific forms of presentation

In one preferred embodiment, the invention provides homogeneous or heterogeneous shaped bodies of known construction.

These include in particular cylindrical tablets which preferably have a diameter of 15 to 60 mm and, more particularly,  $30 \pm 10$  mm. The height  
15 of these tablets is preferably from 5 to 30 mm and more preferably from 15 to 28 mm. Shaped bodies with a diameter of 32, 33, 34, 35, 36, 37, 38 and 39 mm have proved to be particularly favorable. In particular embodiments, the height is 24, 25, 26, 27 or 28 mm.

However, square, rectangular, trapezoidal, oval and irregularly  
20 shaped bases may also be used with advantage. The edge lengths are preferably between 15 and 60 mm and more preferably  $30 \pm 10$  mm.

The weight of the individual shaped bodies, more particularly tablets, is preferably 15 to 60 g and more preferably 20 to 40 g per shaped body or tablet. By contrast, the density of the shaped bodies or tablets normally  
25 assumes values above  $1 \text{ kg/dm}^3$  and preferably in the range from 1.1 to  $1.4 \text{ kg/dm}^3$ .

One or more shaped bodies, for example 2 to 4 shaped bodies, more particularly tablets, may be used according to the particular application, the water hardness range and the nature of the soils to be  
30 removed. Other shaped bodies according to the invention may have even smaller diameters or dimensions, for example around 10 mm.

A homogeneous shaped body in the context of the present invention is understood to be one in which the ingredients of the shaped body - except for the region containing ingredient (I) - are homogeneously distributed in such a way that differences between ingredients and/or active substances are not visible to the naked eye. The granular structure of the solids used is of course still discernible. In one preferred embodiment of the invention, only one other region (phase) is present besides the region containing the ingredient (I).

Accordingly, heterogeneous shaped bodies in the context of the present invention are those in which the ingredients present besides the ingredient (I) do not have to be homogeneously distributed. In one simple case, heterogeneous shaped bodies may be produced, for example, by giving the various ingredients different colors and/or by providing them with different fragrance components.

Another case which, according to the invention, counts as a non-homogeneous (heterogeneous) shaped body is an embodiment in which a shaped body comprising several layers (phases), i.e. at least two layers, besides the region containing the ingredient (I) is compressed. For example, these various layers may have different disintegration and dissolving rates and/or may contain different ingredients. This can result in advantageous performance properties of the shaped bodies. If, for example, ingredients which adversely affect one another are present in the shaped bodies, they can be separated. If a particular sequence of cleaning conditions is to be created in a machine, one (or more) component(s) may be integrated in a (or the) faster disintegrating and/or faster dissolving layer while the other component(s) is incorporated in a (or the) more slowly dissolving layer, so that one component can act in advance or can have already reacted off by the time another component dissolves.

In one preferred embodiment of the invention, another two phases are present besides the region containing the ingredient (I). It is particularly favorable if the ratios by volume of the other two phases are

between 10:1 and 1:10, preferably between 5:1 and 1:5 and more preferably between 2:1 and 1:2.

Another particularly preferred embodiment is characterized in that three or more other phases are present.

5       The layered structure of the shaped bodies may be stack-like, in which case the inner layer(s) dissolve(s) at the edges of the shaped body before the outer layers have completely dissolved or disintegrated. However, the inner layer(s) may also be completely and/or partly surrounded by the layers situated further to the outside which prevents  
10 and/or retards the early dissolution of constituents of the inner layer(s).

In another preferred embodiment of the invention, a tablet consists of at least three layers, i.e. two outer layers and at least one inner layer, at least one of the inner layer(s) containing a peroxy bleaching agent whereas, in the case of the stack-like tablet, the two cover layers and - in  
15 the case of the jacket-like tablet - the outermost layers are free from peroxy bleaching agent. Peroxy bleaching agent and any bleach activators or bleach catalysts and/or enzymes present can also be separated from one another in one and the same tablet and/or shaped body. Embodiments such as these have the advantage that there is no danger of any unwanted  
20 interactions in the shaped bodies according to the invention.

In another favorable and preferred embodiment of the present invention, one of the bleach components or the bleach component, more especially the chlorine component, is not made up in one phase with the perfume component. Another favorable and preferred embodiment of the  
25 invention is characterized in that the silver protector component is not made up with (any of) the bleach component(s). In another favorable and preferred embodiment of the invention, one of the components, or the component, for controlling solubility is made up together with the bleach activator. Another favorable and preferred embodiment of the invention is  
30 characterized in that one of the components, or the component, for controlling solubility is made up together with enzymes. Another favorable

and preferred embodiment of the invention is characterized in that one of the components, or the component, for controlling solubility is made up together with the bleaching agent. Another favorable and preferred embodiment of the invention is characterized in that one of the components, or the component, for controlling solubility is made up together with the silver protector component. Another favorable and preferred embodiment of the invention is characterized in that one of the components, or the component, for controlling solubility is made up together with at least 50% by weight, preferably more than 70% by weight and, more preferably, more than 90% by weight of a surfactant or the surfactant mixture as a whole.

The shaped bodies according to the invention are produced by any of the methods normally used for producing shaped bodies.

In some embodiments, it has proved to be particularly favorable to introduce the region containing the ingredient(s) (I) in the form of a liquid (quite generally a solution and/or melt), optionally at elevated temperature, into a preformed recess of the surrounding ingredients and then to allow this region to solidify by applying conventional technical measures (quite generally drying and/or cooling). A viscosity of more than 1,500 mPas, preferably more than 2,000 mPas, more preferably between 2,000 and 15,000 mPas, most preferably between 2,500 and 7,000 mPas and, in a particularly advantageous embodiment, between 3,000 and 4,000 mPas, has proved to be particularly effective.

It has proved to be particularly effective to combine the ingredient (I) with fusible carrier materials. These include in principle any substances which solidify at or particularly above room temperature.

According to the invention, nonionic surfactants (Dehypon® LT 104, Dehypon® LS 54, Dehydol® LS 30, Lutensol® AT 80), polyethylene glycols with various molecular weights (PEG 400, 12000), soaps (Lorol® C 16), stearates (Cutina® GMS), and also thickened caustic soda and fusible salts, such as sodium carbonate decahydrate, have proved to be



particularly suitable carrier materials. The advantages and disadvantages of the individual ingredients can be reproduced by the expert in tests.

The use of mixtures mentioned in hitherto unpublished **DE 197 27 073**, of which the disclosure is hereby specifically included as part of the present disclosure, is particularly suitable for the purposes of the present application.

In other embodiments, parts of the shaped body and/or components of the shaped body are treated by exposure to microwave radiation in order positively to influence their strength, moisture content and solubility.

However, the constituents may also be simply compressed. In this case, microtabs and shaped bodies smaller in their dimensions than the final shaped body may be used in addition to powders and granules.

#### Specific ingredients

Particular ingredients (I) used in accordance with the invention are oxygen bleaching agents, preferably the alkali metal perborates and hydrates thereof and alkali metal percarbonates, sodium perborate (monohydrate or tetrahydrate) or sodium percarbonate and hydrates thereof preferably being used in accordance with the invention. The persulfates may also be used.

However, other typical oxygen bleaching agents are the organic peracids. Organic acids preferably used include above all the extremely effective phthalimidoperoxycaproic acid although, in principle, any other known peracids may also be used.

Other preferred ingredients (I) are other bleaching agents, for example the halogen bleaching agents mentioned above, among which dichloroisocyanuric acid (DICA) is particularly preferred for the purposes of the invention.

Particular ingredients (I) used in accordance with the invention are bleach activators. Known bleach activators are compounds which contain one or more N- or O-acyl groups, such as compounds from the class of

anhydrides, esters, imides and acylated imidazoles or oximes. Examples are tetraacetyl ethylenediamine (TAED), tetraacetyl methylenediamine (TAMD) and tetraacetyl hexylenediamine (TAHD) and also pentaacetyl glucose (PAG), 1,5-diacetyl-2,2-dioxohexahydro-1,3,5-triazine (DADHT) and isatoic anhydride (ISA).

The bleach activators used may be compounds which form aliphatic peroxocarboxylic acids preferably containing 1 to 10 carbon atoms and, more particularly, 2 to 4 carbon atoms and/or optionally substituted perbenzoic acid under perhydrolysis conditions. Suitable bleach activators are substances which carry O- and/or N-acyl groups with the number of carbon atoms mentioned and/or optionally substituted benzoyl groups. Preferred bleach activators are polyacylated alkylenediamines, more especially tetraacetyl ethylenediamine (TAED), acylated triazine derivatives, more especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, more especially tetraacetyl glycoluril (TAGU), N-acyl imides, more especially N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, more particularly n-nonanoyl or isononanoyloxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, more especially phthalic anhydride, acylated polyhydric alcohols, more especially triacetin, ethylene glycol diacetate, 2,5-diacetoxy-2,5-dihydrofuran, n-methyl morpholinium acetonitrile methyl sulfate (MMA) and the enol esters known from German patent applications **DE 196 16 693** and **DE 196 16 767** and also acetylated sorbitol and mannitol and mixtures thereof (SORMAN), acylated sugar derivatives, more especially pentaacetyl glucose (PAG), pentaacetyl fructose, tetraacetyl xylose and octaacetyl lactose and acetylated, optionally N-alkylated, glucamine and gluconolactone, and/or N-acylated lactams, for example N-benzoyl caprolactam. Combinations of conventional bleach activators may also be used. Bleach activators such as these are present in the usual quantities, preferably in quantities of 1% by weight to 10% by weight and more preferably in quantities of 2% by weight to 8% by weight, based on the

detergent/cleaner as a whole.

In addition to or instead of the conventional bleach activators mentioned above, so-called bleach catalysts may also be incorporated in the shaped bodies. These substances are transition metal salts or  
5 transition metal complexes such as, for example, manganese-, iron-, cobalt-, ruthenium- or molybdenum-salen or -carbonyl complexes. Manganese, iron, cobalt, ruthenium, molybdenum, titanium, vanadium and copper complexes with nitrogen-containing tripod ligands and cobalt-, iron-, copper- and ruthenium-ammine complexes may also be used as bleach  
10 catalysts.

Bleach activators from the group of polyacylated alkylenediamines, more particularly tetraacetyl ethylenediamine (TAED), N-acyl imides, more particularly N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, more particularly n-nonanoyl or isononanoyloxybenzenesulfonate (n- or  
15 iso-NOBS), n-methyl morpholinium acetonitrile methyl sulfate (MMA) are preferably used, preferably in quantities of up to 10% by weight, more preferably in quantities of 0.1% by weight to 8% by weight, most preferably in quantities of 2 to 8% by weight and, with particular advantage, in quantities of 2 to 6% by weight, based on the detergent/cleaner as a whole.

20 Bleach-boosting transition metal complexes, more particularly containing the central atoms Mn, Fe, Co, Cu, Mo, V, Ti and/or Ru, preferably selected from the group of manganese and/or cobalt salts and/or complexes, more preferably the cobalt (ammine) complexes, cobalt (acetate) complexes, cobalt (carbonyl) complexes, chlorides of cobalt or  
25 manganese and manganese sulfate, are also present in typical quantities, preferably in a quantity of up to 5% by weight, more preferably in a quantity of 0.0025% by weight to 1% by weight and most preferably in a quantity of 0.01% by weight to 0.25% by weight, based on the detergent/cleaner as a whole. In special cases, however, more bleach activator may even be  
30 used.

Dishwasher detergents according to the invention may contain

corrosion inhibitors as ingredient (I) to protect the tableware or the machine itself, silver protectors being particularly important for dishwashing machines. Known corrosion inhibitors, for example those described in DE 43 25 922, DE 41 28 672 and DE 43 38 724, may be used. Above all, silver protectors selected from the group of triazoles, benzotriazoles, bisbenzotriazoles, aminotriazoles, alkylaminotriazoles and the transition metal salts or complexes may generally be used. Benzotriazole and/or alkylaminotriazole is/are particularly preferred. In addition, dishwashing formulations often contain corrosion inhibitors containing active chlorine which are capable of distinctly reducing the corrosion of silver surfaces. According to the above documents, chlorine-free dishwashing detergents contain in particular oxygen- and nitrogen-containing organic redox-active compounds, such as dihydric and trihydric phenols, for example hydroquinone, pyrocatechol, hydroxyhydroquinone, gallic acid, phloroglucinol, pyrogallol and derivatives of these compounds. Salt-like and complex-like inorganic compounds, such as salts of the metals Mn, Ti, Zr, Hf, V, Co and Ce are also frequently used. Of these, the transition metal salts selected from the group of manganese and/or cobalt salts and/or complexes are preferred, cobalt(amine) complexes, cobalt(acetate) complexes, cobalt(carbonyl) complexes, chlorides of cobalt or manganese and manganese sulfate being particularly preferred. Zinc compounds may also be used to prevent corrosion of tableware.

Particular ingredients (I) used in accordance with the invention are substances which prevent the resoiling of surfaces and/or which facilitate the separation of soil after a single application (so-called soil-release compounds).

The soil-release compounds used in accordance with the invention include any of the compounds known from the prior art. Particularly suitable are cationic polymers such as, for example, hydroxypropyl trimethyl ammonium guar; copolymers of aminoethyl methacrylate and acrylamide and copolymers of dimethyl diallyl ammonium chloride and

acrylamide, polymers containing imino groups, cationic cellulose derivatives, cationic homopolymers and/or copolymers (monomer units: quaternized ammonium alkyl methacrylate groups).

Particular preference is attributed to the cationic polymers selected  
5 from cationic polymers of copolymers of such monomers as trialkyl ammonium alkyl (meth)acrylate or acrylamide; dialkyl diallyl diammonium salts; polymer-analog reaction products of ethers or esters of polysaccharides with lateral ammonium groups, more particularly guar, cellulose and starch derivatives; polyadducts of ethylene oxide with ammonium groups;  
10 quaternary ethylene imine polymers and polyesters and polyamides containing quaternary lateral groups as soil-release compounds.

Natural polyuronic acids and related substances and also polyampholytes and hydrophobicized polyampholytes and mixtures of these substances are also particularly preferred for the purposes of the  
15 present invention.

According to the invention, between 0 and 5% by weight of enzymes, based on the composition as a whole, may be added to the detergent/cleaner to improve performance or guarantee the same quality of cleaning under milder conditions. The most commonly used enzymes  
20 include lipases, amylases, cellulases and proteases. Preferred proteases are, for example, BLAP® 140 (Biozym), Optimase® M-440 and Opticlean® M-250 (Solvay Enzymes); Maxacal® CX and Maxapem® or Esperase® (Gist Brocades) and even Savinase® (Novo). Particularly suitable celluloses and lipases are Celluzym® 0,7 T and Lipolase® 30 T (Novo  
25 Nordisk). Particularly suitable amylases are Duramyl® and Termamyl® 60 T and Termamyl® 90 T (Novo), Amylase-LT® (Solvay Enzymes) and Maxamyl® P5000 (Gist Brocades). Other enzymes may also be used.

#### Other ingredients

30 In the shaped bodies according to the invention, all ingredients (I) described above can also perform the function of other ingredients should

the condition of the region according to the invention be fulfilled by other ingredients.

Water-soluble and water-insoluble builders may be used in the detergents/cleaners according to the invention, above all to bind calcium and magnesium. Water-soluble builders are preferred because, in general, they tend less to form insoluble residues on tableware and hard surfaces. Typical builders which may be present in quantities of 10 to 90% by weight, based on the composition as a whole, in accordance with the invention are the low molecular weight polycarboxylic acids and salts thereof, the homopolymeric and copolymeric polycarboxylic acids and salts thereof, the carbonates, phosphates and silicates. Water-insoluble builders include the zeolites, which may also be used, and mixtures of the builders mentioned above.

Trisodium citrate and/or pentasodium tripolyphosphate and/or sodium carbonate and/or sodium bicarbonate and/or gluconates and/or silicate builders from the class of disilicates and/or metasilicates are preferably used.

Alkali sources may be present as further ingredients. Alkali sources are alkali metal hydroxides, alkali metal carbonates, alkali metal hydrogen carbonates, alkali metal sesquicarbonates, alkali metal silicates, alkali metal metasilicates and mixtures of the substances mentioned above. According to the invention, alkali metal carbonates, more particularly sodium carbonate, sodium hydrogen carbonate or sodium sesquicarbonate, are preferably used.

A builder system containing a mixture of tripolyphosphate and sodium carbonate is particularly preferred.

Another particularly preferred builder system contains a mixture of tripolyphosphate and sodium carbonate and sodium disilicate.

In principle, any surfactants may be used as surfactants. Nonionic surfactants, above all low-foaming nonionic surfactants, are preferred although other low-foaming surfactants may also be used. Alkoxylated

alcohols, especially ethoxylated and/or propoxylated alcohols, alkyl polyglycosides, and alkyl polyglucamides are particularly preferred.

Alkoxyated alcohols are generally understood by the expert to be the reaction products of alkylene oxide, preferably ethylene oxide, with alcohols, the relatively long-chain alcohols ( $C_{10}$  to  $C_{18}$ , preferably between  $C_{12}$  and  $C_{16}$  such as, for example,  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{14}$ ,  $C_{15}$ ,  $C_{16}$ ,  $C_{17}$  and  $C_{18}$  alcohols) being preferred for the purposes of the present invention. In general, a complex mixture of addition products differing in their degree of ethoxylation is formed from  $n$  moles of ethylene oxide and 1 mole of alcohol, depending on the reaction conditions. Another embodiment is characterized by the use of mixtures of alkylene oxides, preferably a mixture of ethylene oxide and propylene oxide. If desired, "end-capped" alcohol ethoxylates, which may also be used in accordance with the invention, may also be obtained by etherification with short-chain alkyl groups, preferably butyl groups, in a concluding step. According to the invention, highly ethoxylated fatty alcohols or mixtures thereof with end-capped fatty alcohol ethoxylates are particularly preferred for the purposes of the invention.

Alkyl polyglycosides are surfactants which may be obtained by reacting sugars and alcohols using the relevant methods of preparative organic chemistry, a mixture of monoalkylated oligomeric or polymeric sugars being obtained according to the particular method of production used. Preferred alkyl polyglycosides are alkyl polyglucosides. In a particularly preferred embodiment, the alcohol is a long-chain fatty alcohol or a mixture of long-chain fatty alcohols while the degree of oligomerization of the sugars is between 1 and 10.

Fatty acid polyhydroxylamides (glucamides) are acylated reaction products of the reductive amination of a sugar (glucose) with ammonia, long-chain fatty acids, long-chain fatty acid esters or long-chain fatty acid chlorides generally being used as acylating agents. Secondary amides are formed if methyl amine or ethyl amine is used instead of ammonia for the

reduction process, as described for example in **SÖFW Journal**, 119, (1993), 794-808. Carbon chain lengths of C<sub>6</sub> to C<sub>12</sub> are preferably used in the fatty acid moiety.

The regions of the shaped body may be colored. In one particularly preferred embodiment, one or more regions in the shaped body or all the regions in the shaped body are differently colored. In one special embodiment of the shaped body, the color is red. In another special embodiment of the shaped body, the color is green. In another special embodiment of the shaped body, the color is yellow. In another special embodiment of the shaped body, the color is a mixture of different colors.

The storage stability of the shaped body is particularly important. In one particularly preferred embodiment of the invention, the increase in weight of the region of the ingredient (I) during storage under normal domestic conditions, i.e. between 15 and 30°C and between 5 and 55% and preferably between 15 and 35% air humidity for a period of 30 days, preferably 60 days and more preferably 90 days is no more than 50% by weight, preferably no more than 40% by weight, more preferably no more than 30% by weight, most preferably no more than 20% by weight and, in one particularly advantageous embodiment, no more than 10% by weight and, in the most favorable case, no more than 5% by weight.

In another particularly preferred embodiment of the invention, the loss of active substance of the ingredient (I) during storage under normal domestic conditions, i.e. between 15 and 30°C and between 5 and 55% and preferably between 15 and 35% air humidity for a period of 30 days, preferably 60 days and more preferably 90 days is no more than 50% by weight, preferably no more than 40% by weight, more preferably no more than 30% by weight, most preferably no more than 20% by weight and, in one particularly advantageous embodiment, no more than 10% by weight and, in the most favorable case, no more than 5% by weight.

In another particularly preferred embodiment of the invention, the absorption maximum of a 1% solution of a colored region or a colored



component during storage under normal domestic conditions, i.e. between 15 and 30°C and between 5 and 55% and preferably between 15 and 35% air humidity for a period of 30 days, preferably 60 days and more preferably 90 days is no more than 100 wave numbers, preferably no more than 50 wave numbers, more preferably no more than 30 wave numbers, most preferably no more than 20 wave numbers and, in one particularly advantageous embodiment, no more than 10 wave numbers and, in the most favorable case, no more than 5 wave numbers.

#### 10 Examples

The following formulations were mixed and compressed to shaped bodies. The ingredients shown in brackets are examples of the class of compounds in question, but may be replaced by other substances listed in the application. The starting formulations represent preferred ranges of the invention.

In the measurement of effectiveness, the particular ingredient (I) selected was transferred to the region according to the invention. In the other region (other regions), it was reduced in accordance with the invention or left out altogether before the studies were carried out.

20

Possible starting formulation (Ra) and test formulations (Va) (figures = % by weight):

| Ingredient                                 | Ra    | Va1  | Va2  | Va3  | Va4 | Va5 | Va6 | Va7 |
|--------------------------------------------|-------|------|------|------|-----|-----|-----|-----|
| Phosphate (sodium tripolyphosphate)        | 30-60 | 54.8 | 56.4 | 30.5 | 43  | 48  | 48  | 47  |
| Sodium carbonate                           | 5-25  | 15.9 | 13.2 | 21.5 | 7   | 20  | 12  | 24  |
| Sodium disilicate                          | 0-40  | 7.3  | 7.5  | 33.7 | 20  | 3   | 14  |     |
| Polymer (Sokalan CP5)                      | 0-10  | 2.2  | 2.2  |      |     | 1   |     | 5   |
| Sodium metasilicate                        | 0-10  |      |      | 1.8  |     |     |     | 0   |
| Sodium hydrogen carbonate                  | 0-10  |      |      |      | 1   |     | 3   |     |
| Bleach (sodium perborate)                  | 2-20  | 9.0  | 9.0  | 6.7  | 15  | 10  | 12  | 9   |
| Bleach activator (TAED) (co-pentammine-Cl) | 0-5   | 2.1  | 2.1  |      | 3   | 2   | 1   | 1.5 |
| Enzyme (amylase) (Duramyl 60 T)            | 0-5   | 2.0  | 2.0  | 0.7  | 3   | 3   | 3   | 2.5 |
| Enzyme (protease) (Blap 200 S)             | 0-5   | 1.8  | 1.8  | 1.0  | 2   | 2   | 3   | 2.5 |
| Phosphonate or phosphonic acid             | 0-5   | 0.9  | 0.9  |      | 2   |     |     | 1.5 |
| Nonionic surfactant (Dehypon LS 54)        | 0-5   | 2.0  | 2.0  | 2.0  | 2   | 4   | 3   | 1.5 |
| Silver protector (benzotriazole)           | 0-3   | 0.3  | 0.3  | 0    | 0.3 | 0.2 |     | 0.5 |
| Tabletting aid (polyethylene glycol)       | 0-10  |      |      |      |     | 6   |     |     |
| Paraffin (Mp.: 53°C)                       | 0-10  |      | 2.0  | 1.0  |     |     |     | 3   |
| Perfume                                    | 0-1   | 0.2  | 0.2  | 0.2  | 1   | 0.4 | 1   | 0.5 |
| Dye                                        | 0-4   | 1.4  | 1.3  | 1.4  | 0.7 | 0.4 |     | 1.5 |

The builder system of the above starting formulation may also have the following composition (all other ingredients same as for a).

| Ingredient                          | Rb    | Vb1  | Vb2  | Vb3  | Vb4 | Vb5 | Vb6 | Vb7 |
|-------------------------------------|-------|------|------|------|-----|-----|-----|-----|
| Phosphate (sodium tripolyphosphate) | 30-60 | 59   | 56   | 53   | 48  | 48  | 48  | 47  |
| Carbonate (sodium carbonate)        | 5-25  | 21.2 | 20.3 | 22.7 | 17  | 20  | 16  | 24  |
| Polymer (Sokalan CP5)               | 0-10  |      | 2    | 10   | 5   | 4   |     | 5   |
| Sodium metasilicate                 | 0-10  |      |      | 1.8  |     |     |     |     |
| Sodium hydrogen carbonate           | 0-10  |      |      |      | 1   |     | 3   |     |

Examples of another starting formulation (R) according to the present invention and test formulations (V) (% by weight) are shown in the following Table:

| Ingredient                          | Rc    | Vc1 | Vc2 | Vc3 | Vc4 |
|-------------------------------------|-------|-----|-----|-----|-----|
| Phosphate (sodium tripolyphosphate) | 15-35 | 30  | 21  | 35  | 40  |
| Carbonate (sodium carbonate)        | 25-55 | 39  | 50  | 40  | 35  |
| Sodium hydrogen carbonate           | 10-20 | 14  | 19  | 15  | 12  |
| Polymer (Sokalan CP5)               | 0-10  | 3   | 0   |     |     |
| Sodium disilicate                   | 0-10  |     |     |     |     |
| Sodium disilicate                   | 0-10  | 0   | 0   | 0   | 5   |
| Bleach (sodium perborate)           | 2-10  | 7   | 8   | 5   | 5   |
| Bleach activator (TAED)             | 0-5   | 1   | 0   | 1   | 1   |
| Enzyme (amylase) (Duramyl 60 T)     | 0.4-2 | 1   | 0.5 | 0.5 | 0.5 |
| Enzyme (protease) (Blap 200 S)      | 0.4-2 | 1   | 0.5 | 0.5 | 0.5 |
| Phosphonate or phosphonic acid      | 0-5   | 0   | 0   | 0   | 0   |
| Nonionic surfactant (Dehypon LS 54) | 0-5   | 2   | 1   | 1   | 1   |
| Silver protector (benzotriazole)    | 0-3   | 0.5 | 0   | 0.3 | 0   |
| Paraffin (Mp.: 53°C)                | 0-10  | 0   | 0   |     | 0   |
| Perfume                             | 0-1   | 0   | 0   | 0.7 | 0   |
| Dye                                 | 0-4   | 0.5 | 0   | 1   | 0   |

Further examples of a starting formulation (R) according to the present application and test formulations (V) (% by weight) are shown in the following Table:

| Ingredient                          | Rd    | Vd1 | Vd2 | Vd3 | Vd4 |
|-------------------------------------|-------|-----|-----|-----|-----|
| Trisodium citrate                   | 20-55 | 44  | 34  | 44  | 44  |
| Sodium hydrogen carbonate           | 5-35  | 24  | 9   | 34  | 20  |
| Carbonate (sodium carbonate)        | 0-10  | 7   |     |     |     |
| Polymer (Sokalan CP5)               | 0-10  |     | 6   |     |     |
| Sodium disilicate                   | 0-25  |     | 20  |     |     |
| Bleach (sodium perborate)           | 0-22  | 9   | 16  | 17  |     |
| Bleach activator (TAED)             | 0-25  | 3   | 1   | 0   | 20  |
| Enzyme (amylase) (Duramyl 60 T)     | 0.4-5 | 2.5 | 3   | 1   | 5   |
| Enzyme (protease) (Blap 200 S)      | 0.4-5 | 2   | 3   | 1   | 5   |
| Phosphonate or phosphonic acid      | 0-5   | 1.5 | 2.3 |     | 2   |
| Nonionic surfactant (Dehypon LS 54) | 0-5   | 2.5 | 1.7 | 2   | 1   |
| Silver protector (benzotriazole)    | 0-3   | 0.5 | 0.5 |     |     |

| Ingredient           | Rd   | Vd1 | Vd2 | Vd3 | Vd4 |
|----------------------|------|-----|-----|-----|-----|
| Paraffin (Mp.: 53°C) | 0-10 | 3   | 1.5 |     |     |
| Perfume              | 0-1  | 0.9 | 0.5 | 1   | 1   |
| Dye                  | 0-4  | 0.1 | 1.5 |     | 2   |

Further examples of a starting formulation (R) according to the present application and test formulations (V) (% by weight) are shown in the following Table:

| Ingredient                           | Re    | Ve1 | Ve2 | Ve3 | Ve4 |
|--------------------------------------|-------|-----|-----|-----|-----|
| Citrate (trisodium citrate)          | 20-55 | 32  | 36  | 38  | 24  |
| Phosphate (trisodium polyphosphate)  | 20-55 | 26  | 23  | 24  | 24  |
| Carbonate (sodium carbonate)         | 1-15  | 11  | 10  | 11  | 15  |
| Polymer (Sokalan CP5)                | 0-10  |     | 5   | 1.5 | 6   |
| Silicate (sodium disilicate)         | 0-25  | 3   |     |     | 6   |
| Bleach (sodium perborate)            | 2-20  | 16  | 3   | 12  | 9   |
| Bleach activator (TAED)              | 0-5   | 0.5 | 5   | 2   | 3   |
| Enzyme (amylase) (Duramyl 60 T)      | 0-5   |     | 5   | 3   | 2   |
| Enzyme (protease) (Blap 200 S)       | 0-5   |     | 5   | 0.5 | 2   |
| Phosphonate or phosphonic acid       | 0-5   | 2   | 2   |     | 2   |
| Tabletting aid (polyethylene glycol) | 0-10  | 6   | 4   | 5   | 0.8 |
| Nonionic surfactant (Dehypon LS 54)  | 0-5   | 2.5 |     | 2.8 | 2   |
| Silver protector (benzotriazole)     | 0-3   |     |     | 0.2 | 0.2 |
| Paraffin (Mp.: 53°C)                 | 0-10  |     |     |     |     |
| Perfume                              | 0-1   | 1   | 1   |     | 1   |
| Dye                                  | 0-4   | 0   | 1   |     | 1   |

Further examples of a starting formulation (R) according to the present application and test formulations (V) (% by weight) are shown in the following Table:

| Ingredient                          | R1    | V11 | V12 | V13 | V14 |
|-------------------------------------|-------|-----|-----|-----|-----|
| Phosphate (trisodium polyphosphate) | 40-60 | 49  | 49  | 49  | 50  |
| Carbonate (sodium carbonate)        | 0-20  |     | 17  | 19  | 5   |
| Polymer (Sokalan CP5)               | 0-15  | 2   | 4   | 1   | 6   |
| Silicate (sodium disilicate)        | 0-30  | 24  | 6   | 5   | 10  |

| Ingredient                           | R1   | V11 | V12 | V13 | V14 |
|--------------------------------------|------|-----|-----|-----|-----|
| Bleach (sodium perborate)            | 0-15 | 10  | 8   | 10  | 8   |
| Bleach activator (TAED)              | 0-5  | 1.5 | 2   | 3   | 2   |
| Enzyme (amylase) (Duramyl 60 T)      | 0-5  | 2   | 2   | 1.5 | 2.5 |
| Enzyme (protease) (Blap 200 S)       | 0-5  | 3.9 | 2   | 1.5 | 2.5 |
| Phosphonate or phosphonic acid       | 0-8  | 0.8 | 1   | 1   | 2   |
| Tabletting aid (polyethylene glycol) | 0-10 | 0.2 | 4   | 3.7 | 5   |
| Nonionic surfactant (Dehypon LS 54)  | 0-8  | 1.5 | 2   | 4   | 3   |
| Silver protector (benzotriazole)     | 0-5  | 0.1 | 0.5 | 0.3 | 0.5 |
| Perfume                              | 0-2  | 1   | 0.5 | 0.5 | 0.5 |
| Dye                                  | 0-4  | 3   | 2   | 0.5 | 1   |

Further examples of a starting formulation (R) according to the present application and test formulations (V) (% by weight) are shown in the following Table:

| Ingredient                           | Rg    | Vg1  | Vg2  | Vg3  | Vg4 |
|--------------------------------------|-------|------|------|------|-----|
| Phosphate (trisodium polyphosphate)  | 30-60 | 55.7 | 59.6 | 46.5 | 47  |
| Sodium disilicate                    | 5-40  | 22.3 | 17.5 | 39.2 | 24  |
| Polymer (Sokalan CP5)                | 0-10  | 2.2  | 2.2  |      | 5   |
| Sodium metasilicate                  | 0-10  |      |      | 1.8  |     |
| Sodium hydrogen carbonate            | 0-10  |      |      |      |     |
| Bleach (sodium perborate)            | 2-20  | 10   | 10   | 6.7  | 10  |
| Bleach activator (co-catalyst)       | 0-2   | 1.1  | 1.1  |      | 0.5 |
| Enzyme (amylase) (Duramyl 60 T)      | 0-5   | 2.0  | 2.0  | 0.7  | 2.5 |
| Enzyme (protease) (Blap 200 S)       | 0-5   | 1.8  | 1.8  | 1.0  | 2.5 |
| Phosphonate or phosphonic acid       | 0-5   | 0.9  | 0.9  |      | 1.5 |
| Nonionic surfactant (Dehypon LS 54)  | 0-5   | 2.0  | 2.0  | 2.0  | 1.5 |
| Silver protector (benzotriazole)     | 0-3   | 0.3  | 0.3  | 0    | 0.5 |
| Tabletting aid (polyethylene glycol) | 0-10  |      |      |      |     |
| Paraffin (Mp.: 53°C)                 | 0-10  |      | 2.0  | 1.0  | 3   |
| Perfume                              | 0-1   | 0.2  | 0.2  | 0.2  | 0.5 |
| Dye                                  | 0-4   | 1.4  | 1.3  | 1.4  | 1.5 |

Further examples of a starting formulation (R) according to the present

application and test formulations (V) (% by weight) are shown in the following Table:

| Ingredient                           | RH     | Vh1 | Vh2 | Vh3 | Vh4 | Vh5 | Vh6 | Vh7 |
|--------------------------------------|--------|-----|-----|-----|-----|-----|-----|-----|
| Phosphate (sodium tripolyphosphate)  | 30-60  | 40  | 40  | 40  | 45  | 45  | 50  | 35  |
| Sodium metasilicate (5-hydrate)      | 5-45   | 45  | 10  | 40  | 10  | 30  | 20  | 35  |
| Sodium metasilicate (0-hydrate)      | 5-40   | 10  | 10  | 8   | 10  | 8   | 5   | 10  |
| Sodium disilicate                    | 0-40   | 0   | 30  | 0   | 15  | 10  | 5   | 0   |
| Paraffin oil                         | 0-10   | 4   | 5   | 5   | 5   | 6   | 5   | 0   |
| Bleach (trichloroisocyanuric acid)   | 0.5-10 | 1   | 2   | 2   | 3   | 1   | 5   | 5   |
| Enzyme (amylase) (Duramyl 60 T)      | 0-5    |     |     | 1   | 2   |     | 2   | 2   |
| Enzyme (protease) (Blap 200 S)       | 0-5    |     |     | 1   | 2   |     | 2   | 2   |
| Nonionic surfactant (Dehypon LS 54)  | 0-5    |     | 2   | 2   | 2   |     | 2   | 3   |
| Tabletting aid (polyethylene glycol) | 0-10   |     | 1   |     | 4   |     | 2   | 4   |
| Perfume                              | 0-1    |     | 0.3 | 0.3 | 1   |     | 1   | 0.5 |
| Dye                                  | 0-4    |     | 0.7 | 0.7 | 1   |     | 1   | 2.5 |

Another starting formulation (R) (% by weight) and test formulations (V) were tested:

| Ingredient                           | R1    | V1   | V2 | V3  |
|--------------------------------------|-------|------|----|-----|
| Sodium carbonate                     | 35-55 | 43.5 | 45 | 55  |
| Sodium hydrogen carbonate            | 15-35 | 15   | 25 | 34  |
| Polymer (Sokalan CP5)                | 3-10  | 5    | 3  | 0   |
| Sodium metasilicate                  | 0-10  | 3    | 2  | 0   |
| Bleach (sodium perborate)            | 5-12  | 6    | 10 | 8   |
| Bleach activator (TAED)              | 0-5   | 1    | 2  | 0   |
| Enzyme (amylase) (Duramyl 60 T)      | 0.4-2 | 1    | 1  | 0.5 |
| Enzyme (protease) (Blap 200 S)       | 0.4-2 | 1    | 1  | 0.5 |
| Phosphonate or phosphonic acid       | 0-5   | 0    | 2  | 0   |
| Nonionic surfactant (Dehypon LS 54)  | 0-5   | 1    | 2  | 1   |
| Tabletting aid (polyethylene glycol) | 0-5   |      | 3  |     |
| Silver protector (benzotriazole)     | 0-3   | 0.5  | 1  | 0   |
| Paraffin (Mp.: 53°C)                 | 0-10  | 0    | 2  | 0   |
| Perfume                              | 0-1   | 0    | 1  | 0   |
| Dye                                  | 0-4   | 1    | 1  | 1   |

Should a shaped body according to the invention contain several phases, each formulation may also be the constituents of an individual phase, in other words the percentages are then not based - as usual - on the formulation as a whole, but rather on the composition of individual phase.

Each of the formulations may of course also contain other ingredients typical of MDWM (for example fillers, preservatives and the like) in extremely small quantities, in which case the percentage contents of the other ingredients should be varied accordingly.

The production of the shaped bodies according to the invention involves steps which are known to the expert in this field in another connection. A preferred embodiment of the shaped body according to claim 1 contains a recess in a tablet, this recess containing the ingredient

(I). Production is preferably carried out by forming a depression in a shaped body and filling the depression thus formed. The depression may be formed in a Korsch rotary press. In the present case, a Fette tablet press was used. A round tablet die (26 x 36 mm) was selected and, using  
5 a punch, a 5 mm deep recess was formed in one side, the base of the recess being selected so that a volume of 1 ml could be poured in, the surface of the tablet thereafter becoming smooth again.

A liquid mixture of paraffin and an active substance (I) was then poured in and allowed to cool. The cooling process may be assisted by  
10 conventional methods and equipment.

As already mentioned, the ingredient (I) was quantitatively reduced beforehand in accordance with the invention in the corresponding formulation surrounding the filled region and, in the present Examples and studies, was left out in the surrounding regions.

15 In comparisons with homogeneous tablets (where ingredient (I) does not correspond to the invention) and a few commercially available tablets, the tablets according to the invention proved to be superior.

The particular properties of the detergents/cleaners according to the invention were tested by comparison with known detergents/cleaners using  
20 storage stability as an example. The particular properties of the detergents/cleaners according to the invention were tested in comparison with known detergents/cleaners using the removal of tea stains as an example. The particular properties of the detergents/cleaners according to the invention were tested by comparison with known detergents/cleaners  
25 using the removal of enzyme-relevant stains as an example.

In addition, the particular properties of the detergents/cleaners according to the invention were tested by technically untrained people under simulated practical conditions in comparison with homogeneous tablets. Apart from dosing instructions and general safety instructions, the  
30 handling of the detergents/cleaners by the people in question in commercially available dishwashing machines was not influenced in any



way. This comparison test produced particularly good results. The cleaning results were evaluated as particularly favorable.

Particularly good results were obtained when a soil release compound was used as ingredient (I). In a mixture corresponding to formulation Ra or Va1, up to 2% by weight of polyuronic acids, cationic polymers and hydrophobicized polyampholytes were used independently of one another, builder being omitted. The cleaning performance against milk and starch-containing soils in a following wash cycle was between 10 and 30% better than in the case of untreated samples.

10 In another washing test, samples according to starting formulation Ra which contains active chlorine (dichlorocyanurate) as bleaching component on the one hand in homogeneous distribution in the tablet and, on the other hand, in accordance with claim 1, so that the active chlorine was largely separated from the other (particularly enzyme-containing) components, were used. Storage stability after 2 weeks was distinctly poorer in the case of the homogeneous tablet so it was not possible to obtain a satisfactory cleaning effect against milk and starch-relevant stains. This applies to the entirely normal making-up of the bleach component in region (I) which, in the present case, represented a recess. The effect is even clearer where a mixture of chlorine component and paraffin is used in a standard program at 55°C. The cleaning results were better even immediately after production. The effect improved with storage. Tea, milk, burnt-on meat, burnt-in meat, egg and starch mixtures in particular were removed far more effectively than by tablets without a region (I), i.e. with a homogeneously distributed component (I), and commercially available dishwasher tablets.

The effect was discernible even with paraffins having a melting point of 40 to 44°C. The effect is more pronounced with paraffins having a melting point of 46 to 48°C. The cleaning effect is particularly pronounced with paraffins having a melting point of 57 to 60°C.

In another washing test, samples (according to Ra) containing small

quantities of metal catalysts (Mn catalyst, cobalt catalyst (cobalt-pentammine-chloro complex) and, in one case, n-methyl morpholinium acetonitrile methyl sulfate (MMA) as bleach activator component on the one hand in homogeneous distribution in the tablet and on the other hand  
5 in accordance with claim 1, so that the activator component was largely separated from other components (particularly enzyme-containing components), were used. The storage stability after 2 weeks was distinctly poorer in the case of the homogeneous tablet, so that the cleaning effect against milk and starch-relevant stains was far from satisfactory.

10 This applies to the entirely normal making-up of the bleach activator component in region (I) which, in the present case, represented a recess.

The effect is even clearer where a mixture of activator component and paraffin is used in a standard program at 55°C. The cleaning results were better even immediately after production. The effect improved with  
15 storage. Improvements in the removal of tea stains in particular were obtained and milk, burnt-on meat, burnt-in meat, egg and starch mixtures were also removed more effectively than by tablets without a region (I), i.e. with a homogeneously distributed component (I), and commercially available dishwasher tablets.

20 The effect was even discernible with paraffins having a melting point of 40 to 44°C. The effect was more pronounced with paraffins having a melting point of 46 to 48°C. The cleaning effect is also clearly discernible with paraffins having a melting point of 57 to 60°C.

In another test, samples containing surfactants on the one hand in  
25 homogeneous distribution in the tablet and, on the other hand, in accordance with claim 1, so that the surfactant component was largely separated from other components, were used. In this case, the final rinse results were evaluated. Where a mixture of surfactant and paraffin was used in a standard program at 55°C, the results obtained were better than  
30 those obtained with tablets without a region (I), i.e with a homogeneously distributed component (I), and commercially available dishwasher tablets.

The results clearly show that the tablets according to the invention are superior to conventional dishwasher tablets.

In order further to illustrate the advantages of shaped bodies according to the invention, shaped bodies with three regions were produced, the two slower dissolving regions assuming the form of layers. The faster dissolving region according to the invention was obtained by forming the two-layer tablet with a recess, into which the premix for the faster dissolving region was pressed, with the aid of a top punch provided with a projection. Accordingly, the three-phase shaped body according to the invention was produced by the two process steps "formation of two-layer recessed shaped bodies" and "filling of the recess (formation of the faster dissolving region)".

Process step a): formation of recessed shaped bodies:

Two-layer rectangular shaped bodies (weight 20 g) with a recess in the shape of a semiellipse were made by compressing two different premixes. 75% by weight of the shaped bodies consisted of lower phase and 25% by weight of upper phase. The composition in % by weight (based on the particular premix) of the two premixes and hence the two different phases of the recessed shaped body is shown in Table 1 below:

**Table 1:** compositions of the premixes for the upper and lower phases (% by weight)

|                                   | Premix 1<br>(lower phase) | Premix 2<br>(upper phase) |
|-----------------------------------|---------------------------|---------------------------|
| Sodium carbonate                  | 33.0                      | -                         |
| Sodium tripolyphosphate           | 52.0                      | 94.4                      |
| Sodium perborate                  | 10.0                      | -                         |
| Tetraacetyl ethylenediamine       | 1.5                       | -                         |
| Benzotriazole                     | 1.0                       | -                         |
| C <sub>12</sub> fatty alcohol-3EO | 2.5                       | -                         |
| Dye                               |                           | 0.2                       |
| Enzymes                           |                           | 3.0                       |
| Perfume                           |                           | 0.4                       |
| Silicone oil                      |                           | 2.0                       |

If shaped bodies with the composition shown above are introduced into 1 liter of water at 20°C, they dissolve in 20 minutes.

In shaped bodies E according to the invention, citric acid was pressed into the recess of the shaped body as ingredient I. This "citric acid core" formed the faster dissolving region. In Example E1, 1 g citric acid, in Example E2 3 g citric acid and in Example E3 5 g citric acid were pressed into the recess. Since the two layers of the recessed shaped body are free from citric acid, ingredient I is 100% present in the faster dissolving region.

Shaped bodies E1, E2 and E3 were each introduced into a glass beaker filled with 1 liter of water at 20°C. The faster dissolving region dissolved completely in 3 minutes. In order to demonstrate the superiority

of the shaped tablets according to the invention, the detergents E1, E2 and E3 were compared with commercially available dishwasher tablets. To this end, tableware was soiled with tea and the removability of this soil was tested in a 55°C program of a dishwashing machine.

(1) Preparation of the tea soil

In a water purification kettle, 16 liters of cold local water (16°d) were briefly brought to the boil. 96 g of black tea in a nylon net were allowed to draw for 5 minutes with the lid on, after which the tea was transferred to a heated and stirred immersion tank.

60 Tea cups are immersed 25 times at 1-minute intervals in the prepared tea at a temperature of 70°C. The cups are then removed from the hooks and placed face down on a draining board to dry.

(2) Test results

The cleaning performance of the tablets against the tea soil prepared as described in (1) was visually scored by experts on a scale of 1 to 10 where 0 = no cleaning and 10 = complete stain removal.

The tea scores were awarded for washing conditions of 55°C/16°d water hardness in the main wash cycle (i.e. "hard conditions"). The dishwashing machine used was a Miele G 590 (universal program). Table 2 below shows the pH value of the wash liquor after dissolution of the faster dissolving region (\*) and after dissolution of the entire tablet (\*\*) and the tea stain removal achieved:

**Table 2:** removal of tea stains

| Shaped body                               | pH value* | pH value** | Score |
|-------------------------------------------|-----------|------------|-------|
| E1                                        | 8.0       | 9.5        | 6.8   |
| E2                                        | 7.0       | 9.5        | 7.5   |
| E3                                        | 3.0       | 9.5        | 9.5   |
| Commercially available dishwasher tablets | -         | 9.5        | 5.5   |

In other shaped bodies according to the invention, the faster dissolving region was formulated as an effervescent system. To this end, the compositions shown in Table 3 were selected for the faster dissolving region (figures = % by weight):

**Table 3:** composition of the faster dissolving region (% by weight)

|                              | E4   | E5   | E6   | E7   |
|------------------------------|------|------|------|------|
| Citric acid                  | 33.3 | 37.5 | 10.0 | 10.0 |
| Sodium hydrogen carbonate    | 26.7 | 37.5 | 10.0 | 10.0 |
| Enzymes                      | 40.0 | -    | -    | -    |
| TAED                         | -    | 25.0 | -    | -    |
| Sodium perborate monohydrate |      | -    | 80.0 | -    |
| Sokalan® BM-1*               |      |      |      |      |

\* n-methyl morpholinium acetonitrile methyl sulfate (MMA), ca. 50% on a support (BASF)

Three-phase tablets were produced similarly to the preceding Example. The percentages of the individual regions (upper and lower

phases and faster dissolving region) were selected as follows:

**Table 4:** composition of the shaped bodies E4-E6 (% by weight)

|                            | E4   | E5   | E6   | E7   |
|----------------------------|------|------|------|------|
| Lower phase*               | 61.8 | 63.0 | 61.1 | 63.0 |
| Upper phase*               | 29.1 | 29.6 | 28.8 | 29.6 |
| Faster dissolving region** | 9.1  | 7.4  | 10.1 | 7.4  |

\* see Table 1

\*\* see Table 2

In the case of shaped bodies E4 to E7, therefore, the ingredient I confined to the faster dissolving region was always both citric acid and sodium hydrogen carbonate. In the shaped bodies E4, 80.7% of the total enzyme present in the shaped body was contained in the faster dissolving region; in the shaped bodies E7, all the MMA in the shaped body was contained in that region.

In every case, the faster dissolving region dissolved completely in less than 120 seconds, the rest of the tablet taking another 15 minutes in all to dissolve.

The cleaning performance against tea stains in the test described above was also determined for the shaped bodies E4 to E7 by comparison with conventional dishwasher tablets. The results are set out in Table 5.

**Table 5:** removal of tea stains

| Shaped body                               | Score |
|-------------------------------------------|-------|
| E4                                        | 7.8   |
| E5                                        | 8.3   |
| E6                                        | 7.8   |
| E7                                        | 10.0  |
| Commercially available dishwasher tablets | 5.5   |

In further tests, the bleach activator MMA (n-methyl morpholinium acetonitrile methyl sulfate) preferably used in the faster dissolving region was made up as ingredient (I) in shaped bodies differing in composition in which it was 100% present in the faster dissolving region. To this end, one-phase rectangular shaped bodies (weight 24 g) with a recess in the form of a semiellipse were prepared by compressing two different premixes. The composition (in % by weight, based on the particular premix) of the two premixes and hence of the two different recessed tablets is shown in Table 6 below:

**Table 6:** compositions of the premixes for the upper and lower phases (% by weight)

|                              | Premix 3<br>(bleach-containing) | Premix 4<br>(bleach-containing) |
|------------------------------|---------------------------------|---------------------------------|
| Sodium tripolyphosphate      | 50.0                            | 50.0                            |
| Sodium carbonate             | 21.9                            | 32.0                            |
| Sodium disilicate            | 5.0                             | 7.0                             |
| Sodium perborate monohydrate | 10.0                            | -                               |
| Tetraacetyl ethylenediamine  | 2.0                             | -                               |



|                                   | Premix 3<br>(bleach-containing) | Premix 4<br>(bleach-containing) |
|-----------------------------------|---------------------------------|---------------------------------|
| Polycarboxylates                  | 5.0                             | 5.0                             |
| Phosphonates                      | 1.0                             | 1.0                             |
| Benzotriazole                     | 0.1                             | -                               |
| C <sub>12</sub> fatty alcohol-3EO | 2.0                             | 2.0                             |
| Enzymes                           | 3.0                             | 3.0                             |

The bleach-containing recessed tablets made from premix 3 were filled with cores each weighing 1.3 g. The recessed tablets were filled by melting PEG, incorporating the solids and pouring the melt into the preformed recesses or pressing in the pure substances (E12, E13). The composition of the various powder mixtures and hence of the cores is shown in Table 7 which also shows the cleaning performance of the filled core/recess tablets against tea stains prepared in accordance with (1) {for test conditions, see (2)}. The cleaning performance of an unfilled recessed tablet was also determined for comparison (V1). A direct comparison with an ingredient of which no more than 80% was contained in the faster dissolving region of the shaped body was also made (V2). The cores based on pure substances dissolved completely in one minute, the cores based on PEG 1550 took 2 minutes and the cores based on PEG 3000 4 minutes to dissolve completely. The dissolving time of the recess base (rest of the tablet without the dissolved core) was more than 20 minutes in every test.

**Table 7:** composition of the cores (faster dissolving region, % by weight) and cleaning performance of the core/recess shaped bodies

|                        | V1  | V2  | E8  | E9  | E10  | E11 | E12  | E13  |
|------------------------|-----|-----|-----|-----|------|-----|------|------|
| MMA*                   | -   | -   | -   | -   | -    | -   | -    | 100  |
| Sokalan® BM-1**        | -   | -   | 50  | 25  | 44   | 60  | 100  | -    |
| TAED                   | -   | 5-  | -   | -   | -    | -   | -    | -    |
| Sodium perborate       | -   | -   | -   | 25  | -    | -   | -    | -    |
| PEG 1550               | -   | 50  | 50  | 50  | 44   | -   | -    | -    |
| PEG 3000               | -   | -   | -   | -   | -    | 40  | -    | -    |
| PEG 4000               | -   | -   | -   | -   | -    | -   | -    | -    |
| Citric acid            | -   | -   | -   | -   | 4.8  | -   | -    | -    |
| NaHCO <sub>3</sub>     | -   | -   | -   | -   | 7.2  | -   | -    | -    |
|                        |     |     |     |     |      |     |      |      |
| Tea score (55°C/16°dH) | 4.7 | 6.3 | 6.8 | 7.5 | 7.0  | 8.0 | 10.0 | 10.0 |
| Tea score (55°C/3°dH)  | 7.0 | *** | 9.5 | *** | 10.0 | 9.7 | 10.  | 10.0 |

\* n-methyl morpholinium acetonitrile hydrogen sulfate, pure substance

\*\* n-methyl morpholinium acetonitrile hydrogen sulfate (MMA), ca. 50% on a support (BASF)

\*\*\* not measured

Table 7 shows that confining an ingredient to the faster dissolving region is particularly effective if more than 80% of that ingredient is contained in the faster dissolving region (comparison of V2 with E8). It can also be seen that tea stain removal is better, the more quickly the faster dissolving region dissolves compared with the rest of the shaped body.

**CLAIMS**

1. A shaped body containing builders, bleaching agents and surfactants, characterized in that at least one region containing more than 80% by weight, preferably more than 90% by weight, more preferably more than 95% by weight and, most preferably, 100% by weight of an ingredient (I) present which dissolves more than 5%, preferably more than 10%, more preferably more than 25%, most preferably more than 50% and, in one particularly advantageous embodiment, more than 100% faster than the remaining region and/or regions of the shaped body is present.
2. A shaped body as claimed in claim 1, characterized in that the ingredient (I) is a bleaching agent from the group of chlorine and/or oxygen bleaching agents.
3. A shaped body as claimed in claim 1, characterized in that the ingredient (I) is a bleach activator.
4. A shaped body as claimed in claim 1, characterized in that the ingredient (I) is a silver protector and/or a soil-release compound.
5. A shaped body as claimed in claim 1, characterized in that the ingredient (I) is an enzyme and/or a surfactant.
6. A shaped body as claimed in claim 1, characterized in that the ingredient (I) is a component or a compound for controlling solubility.
7. A shaped body as claimed in any of the preceding claims, characterized in that at least one oxygen bleaching agent selected from the group of alkali metal perborates, alkali metal percarbonates, organic peracids and hydrogen peroxide is present.
8. A shaped body as claimed in any of the preceding claims, characterized in that at least one bleaching agent selected from the group of trichlorocyanuric acids, dichloro- or monochlorocyanurates, hypochlorites and other typical chlorine-containing bleaching agents is present.
9. A shaped body as claimed in any of the preceding claims, characterized in that a bleach activator, preferably from the group of polyacylated alkylenediamines, more particularly tetraacetyl ethylene-

- diamine (TAED), N-acyl imides, more particularly N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, more particularly n-nonanoyl or isononanoyloxybenzenesulfonate (n- or iso-NOBS), n-methyl morpholinium acetonitrile methyl sulfate (MMA) and/or bleach-boosting transition metal complexes, more particularly containing the central atoms Mn, Fe, Co, Cu, Mo, V, Ti and/or Ru, preferably from the group of manganese and/or cobalt salts and/or complexes, more preferably the cobalt (ammine) complexes, cobalt (acetate) complexes, cobalt (carbonyl) complexes, chlorides of cobalt or manganese and/or manganese sulfate, is also present.
- 5 10. A shaped body as claimed in any of claims 1 to 9, characterized in that at least one component for controlling solubility is additionally present.
11. A shaped body as claimed in claim 10, characterized in that the component for controlling solubility is a solubility retarder selected from the group of paraffins, microwaxes and high molecular weight polyethylene glycols.
- 15 12. A shaped body as claimed in claim 11, characterized in that the dissolving time of the shaped body as a whole is longer than the duration of the prerinse cycle of a conventional dishwashing machine.
13. A shaped body as claimed in claim 10, characterized in that the component for controlling solubility is a solubility accelerator selected from the group of organic acids, for example citric acid, or a citric acid/bicarbonate mixture and/or celluloses and cellulose derivatives.
- 20 14. A shaped body as claimed in any of the preceding claims, characterized in that one of the bleaching components or the bleaching component, more particularly the chlorine component, is not made up in one phase with the perfume component.
- 25 15. A shaped body as claimed in any of the preceding claims, characterized in that the silver protector is not made up with (any of) the bleaching component(s).
- 30 16. A shaped body as claimed in any of the preceding claims, characterized in that one of the components, or the component, for

controlling solubility is made up together with the bleach activator.

17. A shaped body as claimed in any of the preceding claims, characterized in that one of the components, or the component, for controlling solubility is made up together with the enzymes.

5 18. A shaped body as claimed in any of the preceding claims, characterized in that one of the components, or the component, for controlling solubility is made up together with the bleaching agent.

19. A shaped body as claimed in any of the preceding claims, characterized in that one of the components, or the component, for  
10 controlling solubility is made up together with the silver protector component.

20. A shaped body as claimed in any of the preceding claims, characterized in that one of the components, or the component, for controlling solubility is made up together with at least 50% by weight,  
15 preferably with more than 70% by weight and, more preferably, with more than 90% by weight of a surfactant or the mixture of surfactants as a whole.

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